

OAK RIDGE
National Laboratory

Lithium Halide-Based Superionic Solid Electrolyte and High-Voltage Cathode Interfaces

PI: Robert Sacci
ORNL Team: Teerth Brahmabhatt
SLAC: Jagjit Nanda
U. Houston: Yan Yao, Liqun Guo, Jie Zheng

Email: saccir@ornl.gov
Phone: 865-241-5135

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Approach: The path towards sustainable 500 Wh/kg and 300 cycles

SSBs with Li metal anodes are key to enabling specific energies densities > 400 Wh/kg; however manufacturing and processing costs must be cost effective. This project focuses on synthesis of Li⁺ conducting halide-based solid electrolytes (SEs) and improving stability with high voltage cathodes.

TA: General solution based synthesis route does not work for other Li halide electrolytes. Li3YCl6 (LYC) requires sacrificial additive.

$YCl_3 + LiCl \xrightarrow{H_2O} Li_3YCl_6$

$(NH_4)_3[LYCl_6] + 3LiCl \xrightarrow{Heating} Li_3YCl_6 + 3NH_3 + 3HCl$

Collaboration and Coordination with Other Institutions

SE Membrane and SSB Characterization
Prof. Yan Yao

X-ray scattering Characterization Studies
Jagjit Nanda

Solid State NMR Characterization on Li⁺ transport
Kee Sung

Reviewer-Only Slides

Overview

Timeline

- Project start date: 10/1/2021
- Project end date: 09/30/2026
- Percent complete: 25%

Budget

- FY22: \$250,000
- FY23: \$250,000

Barriers

Performance: Demonstrating (i) SSBs with specific energy 500 Wh/kg over 1,000 cycles and (ii) solid electrolytes with ionic conductivity > 10⁻³ S/cm at room temperature

Interfacial Stability: Developing low cost halide-based solid electrolytes that are stable against Li anodes and high voltage cathodes

Current Density: Achieving ≥2 mA/cm² at room temperature

Partners/Collaborators

- University of Houston
- SLAC

FY22 Recap:

Demonstrated the synthesis and scale up of Li₃InCl₆ (LIC) from alcohol and H₂O solutions above 10 g with >95% purity and > 0.4 mS cm⁻¹

TA: Comparison of synthetic method for LYC shows that solution-synthesized performs better. None require LPSCI bilayer!

Experimental Details
Anode: Li/In Alloy
Separator: LYC (~1 mm)
Cathode: NMC85+C+LYC
Stack Pressure: 50 MPa

Remaining Challenges and Barriers

- Halide SE require high stack pressures to enable cycling at room temperature. Strategies (e.g., cathode adhesion) need to be developed to reduce stack pressure to <10 MPa for practical devices.
- Developing mechanically robust, thin SE separators **at scale** is critical for high energy density. Binder and solvent selection are critical to maintain high ionic conductivity and good interfacial stability. Strategies are needed to synthesize and process thin SE in a roll-to-roll line is needed.
- We need to utilize novel *operando* methods to studying buried interfaces in SSBs to gain insights into interphase evolution and mechanical strain.

Any proposed future work is subject to change based on funding levels

Publications & Presentations – FY 21/22

Conferences & Technical Meetings

- "How Halide sub-lattice affects Li ion transport in antiperovskites and solution phase synthesis of Li Halide electrolytes" R. Sacci and J. Nanda 242nd ECS Meeting, Atlanta GA (Invited)
- "Substituted Argyrodites and halide-based solid electrolytes for all solid-state batteries" R. Sacci and J. Nanda ACS Fall 2022, Chicago IL (Invited)

Peer-Reviewed Journal Publications

Relevance

Impact

- Solid electrolytes (SEs) with high Li⁺ conductivity and that are able to form robust interfaces with electrodes are critical to enable Li metal solid-state batteries (SSBs) for EV applications. Success is the development of a pathway for low-cost roll-to-roll based synthesis/processing by address technical barriers for robust SE-cathode interfaces and improved rate capabilities.

Objectives

The goal is to develop inexpensive, solution-based methods that allow for growing halide-based solid electrolyte (SE) within the porous hi-voltage cathode matrix, leading to a drastic increase in the mechanical robustness and high-rate performance. A key objective is utilizing *in situ* electrochemical and scattering techniques to understand reaction pathways for optimizing ionic transport and interfacial adhesion.

Relevance to VTO Mission

R&D efforts on SEs and interfaces are critical to meet the VTO's long term goal of 500 Wh/kg and 1,000 cycles for EV applications.

TA: Solution-based synthesis of Li3InCl6 can be expanded to alcohol to increase synthesis rate and decrease temperature required with little effect on cycling.

Experimental Details
Anode: Li/In Alloy
Separator: LPSCI+LIC (~1 mm thick)
Cathode: NMC85+C+LIC
Stack Pressure: ~50 MPa

Proposed Future Research

- Improve chemical and redox stability of Li-halide SEs by partial substitution with halides and transition metal cations.
- Optimize composition and architecture of high voltage NMC cathodes that operate at voltages (>4 V vs. Li/Li⁺). Test other low-cobalt Li-ion cathodes such as disordered rocksalt (DRX) cathodes in solid-state batteries.
- Optimize slurry casting procedures to produce sulfide SE layers ≤ 50 μm thick. Thin separators are critical to attain high cell-level energy densities.
- Demonstrate > 2 mA/cm² lithium plating and stripping by optimizing Li-halide SE-Li/In interphase and cell design
- Design < 1 μm thick protective interlayer to enable Li metal anodes.

Any proposed future work is subject to change based on funding levels

Critical Assumptions & Issues

- Lithium Halide-based SEs have high Li⁺ conductivity and are readily synthesizable, but they have narrow electrochemical stability windows, especially on the anodic side. Passive does not occur naturally at the anode/electrolyte interfaces. Strategies to stabilize the electrode/electrolyte interfaces include: (i) adding buffer layers to mitigate SE decomposition and (ii) developing bilayer SE separators which enable independent optimization of Li/SE and cathode/SE interfaces.
- Thin SE layers (≤ 50 μm) are critical to achieve high cell-level energy density. The impact of SE thickness and Li excess on cell performance needs to be studied in more detail. Especially when synthesized particles are 10s of microns in size.
- Electrification of vehicles require SSBs with areal capacities ~5 mAh/cm² that are able to operate at ~10 mA/cm² for 1,000 cycles. Most SEs do not yet meet these criteria.
- Costs will be a major market driver. Robust, thin and in expensive solid electrolytes are needed as well as rapid methods for joining the various electrodes together.

Milestones: FY-22 (Q3-4) and FY-23

Due Date	Description	Status
06/30/2022 (Q3)	Compare conductivity between solvent and mechanical mixing synthesis of Li ₃ InCl ₆ : solution based synthesis should be within 10% of solid state synthesized or better	Completed
09/30/2022 (Q4)	Evaluate all-solid-state battery with best performer with LPS/Li anode: Cycle using Li/In alloy anode and NMC-based cathode. Stretch Goal: Achieve >1 mS/cm at 25°C for solution phase SE from both aqueous and nonaqueous solutions.	Completed
12/30/2022 (Q1)	Demonstration of synthesis of Li ₃ InCl ₆ from other solvents for improved synthesis rate and control (Q1)	Completed
03/30/2023 (Q2)	Compare conductivity between different thin film casting methodologies (Q2)	Completed
06/30/2023 (Q3)	Obtain free-standing SE and SE/Cathode composite films ≤100 μm-thick (Q3)	In Progress
09/30/2023 (Q4)	Demonstrate 50 cycles of SE/NMC-type cathode composites and LPS-coated anodes (Q4)	In Progress

Technical Accomplishments: Bilayer halide/argyrodite electrolyte enables cycling of high voltage, low cobalt NMC85.

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Stack Pressure: ~50 MPa

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Summary

Technical Approach:

- Developed solution-based synthesis routes to produce superior Li-halide based solid electrolytes.

Accomplishments:

- Systematic investigation on synthesis of Li₃InCl₆ and its affects on full cell cycling performance.
- SSB performance is bottlenecked by cathode electrolyte interface and Li metal stability
- NMC/LiCl/Li/In SSBs exhibit stable performance over 50 cycles without applying interfacial buffer layers

Ongoing Work:

- Optimize particle size and cathode distribution.
- Produce thin (<100 μm) halide SE separators using tape-casting methods
- Evaluate SSBs containing laminated SE